[LiCH$_2$SPh(pmdta)]: A Carbenoid

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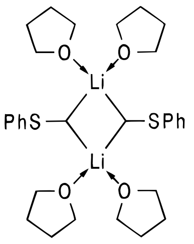
*Summary: The monomeric complex [LiCH$_2$SPh(pmdta)] (**3**; pmdta = N,N,N′,N″,N″-pentamethyldiethylenetriamine), prepared by metalation of PhSCH$_3$ with n-BuLi/pmdta, undergoes in toluene (room temperature, in daylight) extrusion of the methylene group with formation of [LiSPh(pmdta)] and CH$_4$. In refluxing toluene this reaction is thermally induced and the dimerizing α-elimination of **3** proceeds with formation of [LiSPh(pmdta)] and H$_2$C═CH$_2$.*

Since Köbrich's investigations on the stability and reactivity of LiCH$_2$X (X = halide), these highly unstable species have attracted much interest. The thermal instability ($T_{dec} < -100$ °C) is due to the dimerizing α-elimination, which yields ethylene and LiX, a key reaction in the chemistry of lithium carbenoids.[1] Besides the (halomethyl)lithium compounds, carbenoid reactivity of LiCH$_2$YR type compounds (Y = chalcogen; R = alkyl, aryl, H) was found only for Y = O[2] but not for Y = S. Carbenoid reactivity of sulfur-substituted methyllithium compounds has been described so far only for the fully sulfur substituted compound LiC(SPh)$_3$,[3] as well as for phenylthiomethyl[4] and sulfur ylide[5] transition-metal complexes.

Quantum-chemical calculations[6] have revealed that for carbenoid reactivity a three-membered Li−C−Y ring structure seems to be decisive. The formation of such a species is strongly dependent on the degree of aggregation of the lithium reagent and its solvation. Because it had been shown that the THF[7] and the *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda)[8] adducts of LiCH$_2$SPh, **1** and **2**, respectively, are dimeric in the solid state (Chart 1), we decided to prepare the pmdta complex of LiCH$_2$SPh and to investigate its reactivity.

PhSMe reacted quantitatively with *n*-BuLi/pmdta in *n*-pentane at −78 °C to give [LiCH$_2$SPh(pmdta)] (**3**) and [LiSPh(pmdta)] (**4**)/C$_2$H$_4$ in a ratio of about 9:1 (Scheme 1).[9] Crystallization from toluene/*n*-hexane afforded crystals of **3**. Single-crystal X-ray structure determination[10] revealed that crystals of **3** consist of monomeric molecules, as is usual for pmdta complexes of organolithium compounds, LiR(pmdta).[11] The molecular structure of **3** is shown in Figure 1 with selected bond lengths and angles. The C atoms of the two ethanediyl bridges of the pmdta ligand are disordered over two equal positions corresponding to λλ and δδ conformations, respec-

Chart 1



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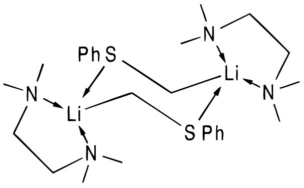

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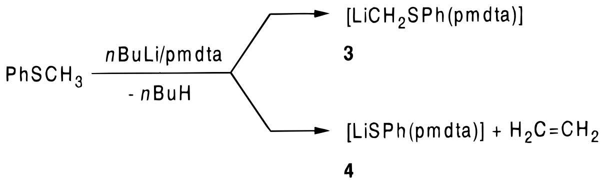
Scheme 1



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(9) *Synthesis*: At 0 °C to a solution of *n*-BuLi (3.9 mmol) in *n*-pentane (10 mL) a solution of pmdta (3.9 mmol) in *n*-pentane (10 mL) was added with stirring. The solution turned yellow and was stirred for 15 min at 0 °C. At −78 °C, PhSCH$_3$ (3.6 mmol) in *n*-pentane (20 mL) was added, leading to the precipitation of a colorless solid (**3**:**4** ca. 9:1; the amount of **4** could be reduced up to 5% when thioanisole was very slowly added), which was filtered, washed with *n*-pentane, and dried in vacuo. Yield: 0.82 g (75%). *Selected spectroscopic data for* **3**: ^{1}H NMR (400 MHz, THF-d_8) δ 0.37 (s, 2H, C*H*$_2$S), 2.24 (s, 12H, N(C*H*$_3$)$_2$), 2.32 (s, 3H, NC*H*$_3$), 2.41 (m, 8H, NC*H*$_2$), 6.69 (t, 1H, *p*-H), 6.99 (t, 2H, *m*-H), 7.28 (d, 2H, *o*-H); ^{13}C NMR (100 MHz, THF-d_8) δ 4.0 (*C*H$_2$S, ^1J(^{13}C,^{1}H) = 121.9 Hz), 44.4 (N*C*H$_3$), 46.1 (N(*C*H$_3$)$_2$), 55.4/58.3 (*C*H$_2$N), 120.8 (*p*-C), 124.2 (*o*-C), 127.7 (*m*-C), 159.0 (*i*-C). The formation of **4** was confirmed by its ^{1}H and ^{13}C NMR data, which are identical with those of an authentic sample prepared from PhSH and *n*-BuLi/pmdta. *Selected spectroscopic data for* **4**: ^{1}H NMR (200 MHz, toluene-d_8) δ 6.82 (t, 1H, *p*-H), 7.00 (t, 2H, *m*-H), 7.64 (d, 2H, *o*-H); ^{13}C NMR: (50 MHz, toluene-d_8) δ 119.1 (*p*-C), 127.4 (*m*-C), 134.8 (*o*-C), 156.0 (*i*-C).

(10) *Crystal data*: **3**, C$_{16}$H$_{30}$LiN$_3$S, M_r = 303.43, monoclinic, space group $P2_1/n$, a = 8.811(2) Å, b = 14.916(6) Å, c = 14.594(3) Å, β = 92.85(2)°, V = 1915.7(9) Å^3, T = 223(2) K, D_c = 1.052 g cm^{-3}, Z = 4, Stoe IPDS diffractometer, Mo Kα radiation, λ = 0.710 73 Å, μ = 0.166 mm^{-1}, 18 279 reflections measured (θ_{min} = 2.69, θ_{max} = 24.99°), 3253 of which are independent (R_{int} = 0.0555), 2514 observed reflections ($I > 2\sigma(I)$), 331 parameters, R = 0.0618 (based on $I > 2\sigma(I)$), R_w = 0.1788 (based on all data), GOF = 1.067, residual electron density 0.315, −0.293 e Å^{-3}. CCDC 145901.

(11) Cambridge Structural Database (CSD), Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge, U.K.

10.1021/om000290s CCC: $19.00

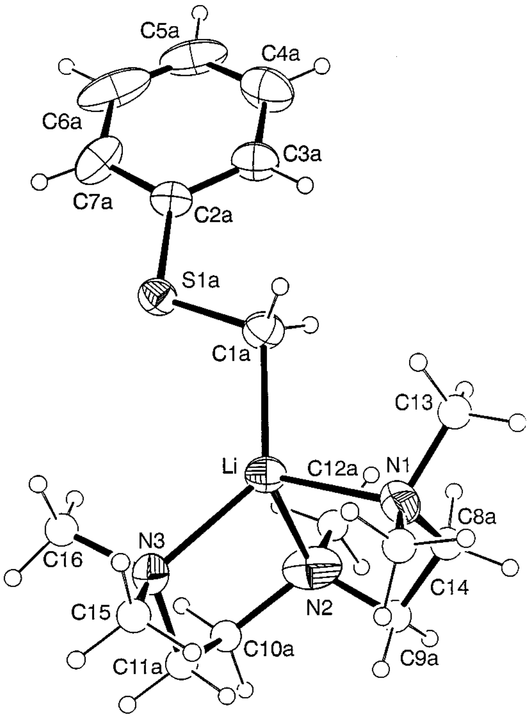
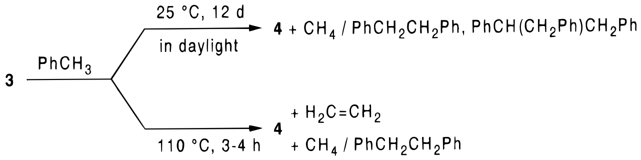


Figure 1. Molecular structure (ORTEP-III plot) in the solid state with atomic labeling scheme for **3**. Thermal ellipsoids are drawn at the 30% probability level; only one position of disordered atoms is displayed. Selected distances (in Å) and angles (in deg): S1−C1 = 1.753(4)/1.75(1), S1−C2 = 1.77(1)/1.81(2), Li−C1 = 2.146(5)/2.20(1), Li−N1 = 2.170(5), Li−N2 = 2.089(5), Li−N3 = 2.138(5); N1−Li−N2 = 86.7(2), N1−Li−N3 = 116.8(2), N2−Li−N3 = 85.4(2), Li−C1−S1 = 114.6(2)/109.5(7), C1−S1−C2 = 111.8(4)/109(1).

tively, of the two chelated rings of ethylenediamine. Obviously, due to great flexibility within the packing, the $PhSCH_2$ group is disordered over two positions with an occupancy of 76:24. The lithium environment [LiN_3C] is distorted tetrahedral with two relatively small $N_{terminal}$−Li−$N_{central}$ angles (85.4(2), 86.7(2)°), as is common for organolithium pmdta complexes (range 79(2)−87.4(7)°[11]). The organic group is bent away from one of the two terminal N atoms (C1a−Li−N3 = 130.2(3)°/C1b−Li−N1 = 136.6(4)°).[12] The structure of the $PhSCH_2$ group in **3** is very similar to those in the dinuclear complexes [$Li_2(CH_2SPh)_2(THF)_4$] (**1**) and [$Li_2(CH_2SPh)_2(tmeda)_2$] (**2**). As in **2** and in other lithiated thioethers[13] the S−CH_2 bond (**3**, 1.753(4)/1.75(1) Å; **2**, 1.759(2) Å) is significantly shorter than expected for an S−C(sp^3) bond (median, 1.817 Å; lower/upper quartile (q_l/q_u), 1.809/1.827 Å[14]). Compound **3** is the first complex of the type [$LiCH_2YR_n(L)$] with a Lewis basic heteroatom Y which is monomeric in the solid state. Until now, monomeric complexes were found only of more highly substituted compounds such as, for example, [$LiCHCl_2(py)_3$], [Li{$CHSiMe_3(PMe_2)$}(pmdta)], and [Li{CHPh(SPh)}$(THF)_3$].[15]

Scheme 2



The ^1H and ^{13}C NMR data in THF solution of the $PhSCH_2$ moiety in complex **3** are identical with those in complexes **1** and **2**. Also, the magnitude of the $^1J(^{13}C,^1H)$ coupling constant of the CH_2 group (121.9 Hz) is the same as those of **1** (121.0 Hz)[7] and **2** (121.4 Hz).[8] The isotopically labeled complex [$^6Li^{13}CH_2SPh$(pmdta)] (**3***) (prepared from $PhS^{13}CH_3$ and n-Bu^6Li/pmdta) exhibits a 1:1:1 triplet for the methylene carbon resonance in THF at −100 °C. Because of line broadening ($b_{1/2}$ ca. 26 Hz) the ^6Li signal (δ ca. 0.5 ppm) is not split even at −90 °C. The coupling constant $^1J(^{13}C,^6Li)$ is nearly the same (10.4 Hz) as that in **2*** (9.2 Hz).[8] The triplet pattern shows that only one Li (^6Li: $I = 1$) is bound to the methylene carbon atom. This is in agreement with a monomeric structure in solution as found in the solid state, although a dimeric structure with the six-membered ring [$Li_2C_2S_2$], as found in the tmeda complex **2**,[8] cannot be strictly ruled out.

Freshly prepared solutions of **3** in toluene-d_8 show the expected ^1H and ^{13}C NMR spectra ($\delta(CH_2)$ 0.37 ppm, $\delta(CH_2)$ 4.0 ppm). At room temperature, within a few hours a H/D exchange reaction takes place, forming [LiCHDSPh(pmdta)] (24 h, 0.6 m, ca. 20%). This reaction probably is a polar process and proceeds so smoothly because toluene can be easily metalated by the monomeric **3**. In the dark no change of color of the toluene solution was observed. In daylight a toluene solution of **3** turns deep violet and then pale orange. At this point **3** has been converted completely (25 °C, 0.88 m, 12 days) to [LiSPh(pmdta)] (**4**) with formation of methane (besides ca. 1% of a mixture of ethane, n-butane, and isobutane) and a mixture of $PhCH_2CH_2Ph$ and $PhCH(CH_2Ph)CH_2Ph$ in a ratio of about 5:4 (Scheme 2).

Compound **3** is soluble in THF, benzene, and toluene, forming pale yellow solutions. In refluxing THF within 3−4 h no decomposition occurred; in refluxing benzene only very little decomposition was observed. However, in refluxing toluene an intense dark green solution was formed and after a few hours **3** was completely converted to [LiSPh(pmdta)] (**4**), with formation of ethylene and methane (ca. 70:30) (cf. Scheme 2). Furthermore, 1,2-diphenylethane was formed in about 15% yield, based on **3**. No further organosulfur products were detected. PhSSPh, $PhSCH_2SPh$, and $PhSCH_2CH_2SPh$, which are observed in radical reactions of $PhSCH_2^{\bullet}$ [16] or those ($PhSCH_2CH_2Ph$, $PhSCH_2Ph$) which can be expected as coupling products between $PhSCH_2^{\bullet}$ and toluene, were not formed.

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(12) Here and in the following the values for the major and minor occupied positions are separated by a slash.

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Transfer of the methylene group in [$LiCH_2SPh$(pmdta)] (**3**) to cyclohexene to produce norcarane (toluene, 110 °C; **3**:cyclohexene = 1:5) was not observed. This also was the case for $LiCH_2Cl$ in THF/ether, but in pentane norcarane was formed.[17] The formation of **4**/C_2H_4 from **3** according to Scheme 2 is a dimerizing α-elimination that is typical for lithium carbenoids $LiCH_2YR_n$ (YR_n = Hal,[17] OR^2). The photolytic (daylight) and thermal decomposition of **3** in toluene, yielding **4**/(CH_4, $PhCH_2CH_2Ph/PhCH(CH_2Ph)CH_2Ph$), involves a double H abstraction from toluene and from $PhCH_2CH_2Ph$, respectively, by the methylene group. Thus, the reactivity of **3** can be regarded as that of a "triplet carbenoid" in analogy to that of triplet methylene,[18] but at his point this is only speculation.

[$LiCH_2SPh$(pmdta)] (**3**) can be regarded as a lithium carbenoid, but there is no evidence for such a formulation, either in its structural parameters[13] ($LiCH_2-S$ bond elongation) in the solid state or in its NMR parameters[13] (methylene carbon low-field shift and smaller ^1J(C,H) coupling constants) in solution. This suggests that **3** is the precursor of the "real" carbenoid[19] formed by decoordination of at least one terminal nitrogen atom of the pmdta ligand (as shown by NMR spectroscopy for [Li{CHPh(SPh)}(pmdta)] in ref 20) and coordination of sulfur to lithium.

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Supporting Information Available: Tables giving details of the X-ray crystal structure investigation of **3** and text and figures giving synthetic details and spectroscopic data for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[19] DFT calculations for monomeric $LiCH_2SMe$ show two C_1-symmetrical structures (**a**, **b**) with Li−C−S rings (**a**/**b**: Li−C, 1.956/1.933 Å; Li−S, 2.308/2.322 Å; CH_2-S, 1.831/1.897 Å; $Li-C-S-C_{Me}$, 127.1/87.9°) of similar energy ($E_{\mathbf{a}} - E_{\mathbf{b}} = -0.6$ kcal/mol). Only structure **b** shows the typical features of a carbenoid, namely a low-field shift by 11 ppm (GIAO calculations) of the methylene carbon atom and an elongation of the C−S bond by 0.070 Å in comparison with those in Me_2S (calculated at the same level).

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